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Nuclear Magnetic Resonance Spectroscopy.
Cyclopropane Derivatives.

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Nuclear Magnetic Resonance Spectroscopy.

Cyclopropane Derivatives.¹

(1) Supported in part by the Office of Naval Research and the National Science Foundation.

By Dinshaw J. Patel,² M. E. H. Howden and John D. Roberts

(2) J. N. Tata Fellow, 1961-1963.

Chemical shifts and coupling constants have been determined from the analysis of proton nuclear magnetic resonance spectra for a series of cyclopropane derivatives. The geminal and vicinal cyclopropyl couplings have opposite signs. Additional ¹³C-H coupling constants have been obtained for cyclopropanes which support the conclusion that the hybridization of the carbon bonding orbitals in cyclopropanes is close to sp^2 . The chemical shifts for several cyclopropane hydrocarbons seem consistent with a ring-current effect.

Proton n. m. r.³ and fluorine n. m. r.⁴ spectroscopy have been

(3) G. L. Closs, R. A. Moss and J. J. Coyle, J. Am. Chem. Soc., 84, 4985 (1962).

(4) W. Mahler, J. Am. Chem. Soc., 84, 4600 (1962).

utilized for structure determinations of substituted cyclopropanes.
Coupling constants and chemical shifts of cyclopropane derivatives^{5, 6}

(5) H. M. Hutton and T. Schaefer, Can. J. Chem., 40, 875 (1962).

(6) J. D. Graham and M. T. Rogers, J. Am. Chem. Soc., 84, 2249 (1962).

have recently been reported and interpreted in terms of substituent effects and molecular geometries.⁶

In the present research, the spin-spin splittings in the proton n. m. r. spectra of several substituted cyclopropanes have been analyzed using standard methods^{7, 8} with results shown in Table I.

(7) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in Nuclear Magnetic Resonance," W. A. Benjamin, Inc., New York, 1961.

(8) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, 1959.

The Wiberg,⁹ the Bothner-By and the Swalen¹⁰ computer

(9) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, 1962.

(10) J. D. Swalen and C. A. Reilly, J. Chem. Phys., 37, 21 (1962).

programs were used to obtain the best agreement between the observed and the calculated spectra. The AB cyclopropyl proton patterns in the n. m. r. spectra of tetrasubstituted cyclopropanes yielded the cyclopropyl coupling directly. The trans-cyclopropyl couplings in the ABX type spectra of trans-3-(trans-2'-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid and its dimethyl ester were determined directly from the AB portion of the spectrum, the downfield part of which was split by the adjacent vinyl hydrogen. The n. m. r. spectra of neat samples of 1,1-dimethylcyclopropanecarboxylic acid, dimethyl 1-methylcyclopropane-cis-1,2-dicarboxylate and dimethyl 1-methylcyclopropane-trans-1,2-dicarboxylate were analyzed as ABC systems. Identification in the observed spectrum of the three quartets and repeated spacings between lines gave approximate values of the chemical shifts and coupling constants, respectively. Best calculated frequency fits for the four possible combinations of relative signs of couplings were then obtained using the Swalen program.¹⁰ The best fit between observed and calculated intensities was found for the assignments with geminal coupling having an opposite sign to the vicinal couplings in the three ABC systems studied. The analysis of the n. m. r. spectrum of dimethyl 1-methylcyclopropane-trans-1,2-dicarboxylate in benzene gave magnitudes and signs of couplings in agreement with the neat compound.

The ¹³C satellite n. m. r. spectra of 1,1-dichlorocyclopropane, 1,1-dimethylcyclopropane, spiropentane and spirohexane were analyzed as AA'XX' systems. The center of each multiplet of the ¹³C satellites was determined by the moment method.¹¹ Similar calculated spectra in

(11) W. Anderson and H. M. McConnell, J. Chem. Phys., 26, 1496 (1957).

agreement with the observed spectrum were found for the geminal coupling having either the same or opposite sign to the vicinal couplings. The geminal couplings were assigned opposite signs to the vicinal couplings in these AA'XX' systems on the basis of evidence for the ABC and AA'BB' type proton spectra of substituted cyclopropanes. The cis and trans couplings which have the same signs, are interchangeable without affecting the spectrum. The errors involved in the determination of coupling constants are large due to a high signal-to-noise ratio in the observed spectrum, and also because small changes in the geminal coupling do not have much effect on the calculated spectrum.

The AA'BB' type proton n. m. r. spectrum of neat 1-phenyl-1-bromocyclopropane was solved with the aid of the Swalen program. The only satisfactory fit was obtained with the geminal coupling taken to have the opposite sign to the vicinal couplings. Interchange of the two cis couplings and interchange of the geminal and trans couplings does not affect the calculated spectrum. The assignment of geminal and trans couplings with opposite signs appears to be definite and is supported by analysis of the spectrum of 1-phenyl-1-bromocyclopropane in chloroform (where the chemical shifts are different).

Gutowsky and co-workers¹² on the basis of valence-bond calcu-

(12) H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys., 31, 1278 (1959).

lations have predicted a positive geminal coupling for H-C-H angles less than 120°. However, a recent publication¹³ on the proton n. m. r.

(13) E. Lustig, J. Chem. Phys., 37, 2725 (1962).

spectra of small-ring compounds, indicates that the geminal coupling has an opposite sign to the vicinal couplings in cyclobutane derivatives. With the aid of spin decoupling, Anet¹⁴ has shown that the geminal

(14) F. A. L. Anet, J. Am. Chem. Soc., 84, 3767 (1962).

proton-proton coupling in CHD_2OH is opposite in sign to the $^{13}\text{C}-\text{H}$ coupling. Since the latter coupling is almost sure to be positive,¹⁵

(15) M. Karplus, J. Am. Chem. Soc., 84, 2458 (1962).

the geminal coupling must have a negative sign. On the basis of this evidence we have assigned the geminal coupling a negative sign and the cis and trans vicinal couplings positive signs in cyclopropanes. It is very interesting that in ethylene oxides, the coupling constants have been reported to have the same relative sign.¹⁶

(16) C. A. Reilly and J. D. Swalen, J. Chem. Phys., 32, 1378 (1960); C. A. Reilly and J. D. Swalen, J. Chem. Phys., 35, 1522 (1961).

The geminal H-C-H angles in cyclopropanes appear to fall in the vicinity of $114.5 - 118^\circ$ ¹⁷ and, for this range of angles, the

(17) E. Goldish, J. Chem. Ed., 36, 408 (1959).

theoretical valence-bond curve of Gutowsky and co-workers¹² predicts H-C-H spin-spin couplings of +4.5 to +7 cps. We have investigated the coupling constants in a number of cyclopropanes with different kinds of substituent groups and find the geminal coupling constants between -3.1 to -5.9 cps (Table I). These results contrast with those of Weitkamp and co-workers¹⁸ who report geminal couplings of 7.0

(18) H. Weitkamp, U. Hasserodt and F. Korte, Chem. Ber., 95, 2280 (1962).

to 9.0 cps for substituted 1,1-dichlorocyclopropanes. In monosubstituted epoxides, the geminal coupling constants have been reported¹⁶ to fall in a narrow range of +5.0 to +6.3 cps for the compounds studied. In ethylene oxides, the H-C-H angle is around 116° and similar geminal couplings in cyclopropanes and ethylene oxides would be expected due to the dependence of the coupling on H-C-H angle. The valence-bond calculations of Karplus¹⁹ and the molecular-orbital treatment of Conroy²⁰

(19) M. Karplus, J. Chem. Phys., 30, 11 (1959).

(20) H. Conroy, Advances in Organic Chemistry, Vol. 2, Interscience Publishers, Inc., New York, 1960.

predict for sp^3 hybridization, a dependence of the vicinal coupling constant on the dihedral angle between the C-H bonds. For the geminal H-C-H angles of 114.5 - 118° for cyclopropanes¹⁷ the corresponding dihedral angles are calculated to be 131 - 134° for trans cyclopropyl hydrogens and 0° for cis cyclopropyl hydrogens. The Karplus

equations predict for these dihedral angles, a cis coupling of +8.2 cps and a trans coupling of +3.8 to +4.3 cps, while the Conroy curve predicts cis and trans couplings of +8.0 cps and +6.4 to +7.0 cps, respectively. The vicinal cyclopropyl coupling constants (Table I) are found to be +8.0 to +11.2 cps for cis hydrogens and +5.2 to +8.0 for trans hydrogens in cyclopropanes. The cis coupling was found to be greater than trans in cyclopropanes in agreement with theory. In monosubstituted ethylene oxides,¹⁶ the cis and trans couplings have smaller magnitudes than in cyclopropanes being +4.0 to +5.2 cps and +1.86 to +2.51 cps for cis and trans protons. The cis hydrogens in both cyclopropanes and ethylene oxides are eclipsed and the difference in couplings cannot be accounted for on the basis of dihedral angle. The differences in vicinal couplings may be due to the electronegativity of oxygen in the oxides. Lynden-Bell and Sheppard²¹

(21) R. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. (London), A269, 385 (1962).

have analyzed the proton n. m. r. spectra of ¹³C-labeled acetylene, ethylene and ethane and found the ¹³C-H coupling to be 249, 156.3 and 125 cps respectively. The fact that the ¹³C-H values for cyclopropanes (Table I) fall between 157.8 and 166.5 cps reinforces the suggestion²² that the hybridization of the carbon bonding

(22) N. Muller and D. E. Pritchard, J. Chem. Phys., 31, 768 (1959).

orbitals in cyclopropanes is close to sp². The ¹³C-H couplings in

cyclopropanes may be compared with those observed for allenes²³

(23) E. B. Whipple, J. H. Goldstein and W. E. Stewart,
J. Am. Chem. Soc., 81, 4761 (1959); E. I. Snyder and J. D. Roberts,
J. Am. Chem. Soc., 84, 1582 (1962).

which are in the range 166-168 cps and with those for three-membered heterocycles²⁴ which are in the range 168-176 cps. The ¹³C-F

(24) F. S. Mortimer, J. Mol. Spect., 5, 199 (1962).

coupling in octafluorocyclobutane²⁵ is 298.0 cps. We find for the

(25) R. K. Harris, J. Phys. Chem., 66, 768 (1962).

¹⁹F spectrum of hexafluorocyclopropane a ¹³C-F coupling of 328.7 cps and a 6.4 cps upfield ¹³C isotope effect on the fluorine line positions. Not enough data is available to use the magnitude of ¹³C-F coupling in fluorocyclopropanes to indicate the hybridization of the carbon-bonding orbitals.

A study of chemical shifts in cyclopropanes offers the possibility of giving new insight into the electronic structure of the cyclopropane ring. A large body of evidence has accumulated which supports the concept that the cyclopropane ring system possesses double-bond character.²⁶ The evidence is based on measurements of dipole

(26) See, for example, E. Vogel, Angew. Chem., 72, 4 (1960).

moments, ultraviolet and infrared spectra, and ionization potentials as well as on chemical reactivity. Cyclopropane has been suggested

by Walsh²⁷ to have bonding corresponding to a three-centered ethylene--

(27) A. D. Walsh, Trans. Faraday Soc., 45, 179 (1949).

the C-C bonds being formed by overlap in the plane of the ring of p orbitals on neighboring carbon atoms and by overlap of three sp² orbitals on adjacent carbon atoms directed towards the center of the ring (Figure 1). The Walsh model assumes that two electrons occupy the central hybrid orbitals while four electrons occupy the molecular orbitals formed by overlap of the p-atomic orbitals. Some localized bond character was predicted for cyclopropane leading to hybridization between sp³ and sp² but closer to sp². On the basis of a pure valence-state model with perfect pairing, Coulson and Moffitt²⁸

(28) C. A. Coulson and W. E. Moffitt, Phil. Mag., 40, 1 (1949).

formulate the carbon-carbon bonds of cyclopropane to involve hybrid orbitals which lie outside the internuclear angles. It was shown that the most favorable hybridization angle corresponds to having the C-C bond-forming orbitals at an angle of 104° which make the difference between internuclear lines and the hybrid orbitals be 22° (Figure 1). The Coulson-Moffitt model predicts the C-H bond orbitals in cyclopropane to have less p-character than normal tetrahedral bonds and hence be more like ethylene than ethane.

Despite the fact that the theoretical models indicate that the C-H bonds in cyclopropane should be more closely akin to those of ethylene than those of ethane, the cyclopropyl resonances come very

significantly upfield from the vinyl resonances. Clearly some factor(s) other than carbon hybridization determine the chemical shifts of cyclopropyl hydrogens. Comparison of the cyclopropyl chemical shifts for 1,1-dimethylcyclopropane, spiropentane and spirohexane indicate that as the external C-C-C bond angle is decreased the cyclopropyl resonances are shifted to lower field. (see Table I).

The contribution of magnetic anisotropy²⁹ of the C-C bonds in

(29) H. M. McConnell, J. Chem. Phys., 27, 226 (1957).

cyclopropanes to the proton shielding has been calculated by Wiberg and Nist³⁰ to be 15 cps. The greater mobility of the carbon electrons

(30) K. B. Wiberg and B. J. Nist, J. Am. Chem. Soc., 83, 1226 (1961).

in cyclopropane predicted on the basis of the theoretical models compared to ordinary saturated compounds suggests that part of this anomalous diamagnetic shift may be due to a cyclopropane ring-current effect. This could either oppose or reinforce the field of the magnet depending on the position of the attached hydrogen atom relative to the ring.

Johnson and Bovey³¹ have calculated the chemical shift changes in

(31) C. E. Johnson, Jr., and F. A. Bovey, J. Chem. Phys., 29, 1012 (1958).

aromatic systems due to ring current effects by considering the circular precession of the π electrons in two regions above and below the plane of the aromatic ring under the influence of the component of the applied field which is perpendicular to this plane.

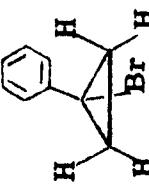
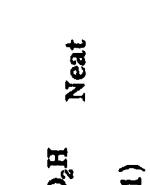
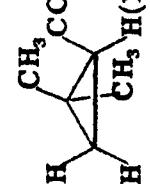
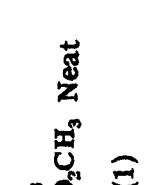
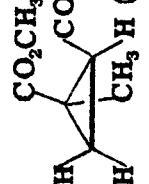
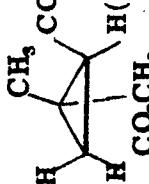
The Johnson and Bovey method³¹ was applied to the calculation of expected chemical shifts for ring and side-chain hydrogens in several cyclopropanes. The mobile electrons, four for the Walsh model and six for the Coulson and Moffitt model, were assumed to precess in the plane of the cyclopropane ring. Molecular parameters given by Goldish¹⁷ were used. Calculations were carried out for (Case A) the radius of the ring current equal to that of the circle circumscribing the ring (0.88 Å for cyclopropane) and (Case B) of a circle passing through the center of maximum electron density (assumed to 0.5 Å from the carbon atom) of a p orbital oriented as in the Walsh model (1.01 Å for cyclopropane). The results are summarized in Table II and compared with observed shifts.

The calculated values are in no more than qualitative agreement with the observed chemical-shift differences. Since some degree of localization of the C-C bond electrons in cyclopropane is likely, the calculated influence of ring currents probably represents upper limits of such effects. It is to be expected that the C-C and C-H bond anisotropies also make substantial contributions to the observed chemical shifts. The assumed ring-current for cyclopropane suggests that a hydrogen located near the equatorial plane of the ring will experience a paramagnetic effect on its resonance position and a diamagnetic effect is predicted for hydrogens inside the ring, or somewhere above it and reasonably close to its three-fold axis. The comparison between experiment and theory shown in Table II cannot be taken as establishing the existence of ring current in cyclopropanes, but the trends are reasonably consistent with a ring-current effect which has also been invoked to

explain the unusually large molar diamagnetic susceptibility of cyclo-
propane.³²

(32) J. R. Lacher, J. W. Pollock and J. D. Park, J. Chem. Phys.,
20, 1047 (1952).

TABLE I
COUPLING CONSTANTS AND CHEMICAL SHIFTS IN CYCLOPROPANE DERIVATIVES

| Compound | Formula | Solvent | Coupling Constants cps | | Chemical Shifts cps δ | | |
|--|--|--|------------------------|-------------------|------------------------------|--------|--------------------------|
| | | | J_{gem} | J_{cis} | J_{trans} | H(1) | H(2) |
| 1-Phenyl-1-bromo-cyclopropane | (2)  (3)  | Neat ^b | -5. 9 \pm 0. 2 | +10. 5 \pm 0. 3 | +7. 0 \pm 0. 2 | -- | 53. 1 ^a 70. 1 |
| 1, 1-Dimethylcyclopropanecarboxylic acid | (2)  (3)  | Neat | -4. 3 \pm 0. 3 | +8. 0 \pm 0. 3 | +5. 6 \pm 0. 3 | 83. 4 | 58. 4 47. 5 |
| Dimethyl 1-methyl-cyclopropane- <u>cis</u> -1, 2-dicarboxylate | (2)  (3)  | CO ₂ CH ₃ CO ₂ CH ₃ Neat | -4. 7 \pm 0. 2 | +8. 6 \pm 0. 2 | +6. 3 \pm 0. 2 | 115. 4 | 98. 9 69. 1 |
| Dimethyl 1-methyl-cyclopropane- <u>trans</u> -1, 2-dicarboxylate | (2)  (3)  | CO ₂ CH ₃ CO ₂ CH ₃ Neat ^c | -4. 2 \pm 0. 2 | +8. 8 \pm 0. 2 | +6. 6 \pm 0. 2 | 133. 4 | 72. 1 88. 8 |

| Compound | Formula | Solvent | Coupling Constants cps | | | | shift cps h |
|---------------------------|---------|----------------------------|---|-------------|-------------|-----------------------------------|----------------|
| | | | J_{gem} | J_{cis} | J_{trans} | J_{sCH} | |
| 1, 1-Dichlorocyclopropane | | Benzene | -4. 5±1. 0 ^d (+1. 5±1. 0) | +11. 2±0. 5 | +8. 0±0. 5 | 166. 5 | 88. 2 |
| 1, 1-Dimethylcyclopropane | | Benzene | -4. 5±1. 0 ^d (+2. 6±1. 0) | +9. 2±0. 5 | +5. 4±0. 5 | 158. 7 | 12. 0 |
| Spiropentane | | Benzene | -3. 9±1. 0 ^d (+2. 4±1. 0) | +8. 9±0. 5 | +5. 2±0. 5 | 159. 8 ^e | 43. 8 |
| Spirohexane | | Benzene | -5. 1±2. 0 ^d (+2. 3±2. 0) | +9. 7±0. 5 | +6. 3±0. 5 | 157. 8 | 20. 4 |
| Cyclopropane | | 5% w/v in CCl ₄ | | | | 161. 8 ^f | 13. 2 |
| Hexafluoro-cyclopropane | | CFCl ₃ | | | | J_{3CF} 897±122 ^g | 328. 7 |

| Compound | Formula | Solvent | Coupling Constants cps | | |
|--|---------|----------------|-------------------------------|------------------|--------------------|
| | | | J_{gem} | J_{cis} | J_{trans} |
| 1, 3, 4, 5-Tetramethyl-2-methylene- <u>bicyclo</u> -[3.1.0]hex-3-ene | | Neat | (-) 3.1 ± 0.2 ^d | | |
| Dimethyl-1, 2-dimethyl-cyclopropane- <u>cis</u> -1, 2-dicarboxylate | | Neat | (-) 4.2 ± 0.2 ^d | | |
| 2-Oxa-7, 7-dichloro-norcarane | | 5% w/v in CCl4 | (+) 8.6 ± 0.2 | | |
| 2, 2-Dimethyl- <u>cis</u> -3-phenylcyclopropane-1-carboxylic acid | | sat. in CHCl3 | (+) 9.1 ± 0.2 | | |

Coupling Constants

| Compound | Formula | Solvent | J_{gem} | J_{cis} | J_{trans} |
|---|---------|-------------------------|------------------|------------------|----------------------|
| 2, 2-Dimethyl- <u>trans</u> -3-phenylcyclopropane-1-carboxylic acid | | Sat. in CHCl_3 | | | $(+). 7 \pm 0.2^1$ |
| 2, 2-Dimethyl- <u>trans</u> -3-phenylcyclopropane-1-carboxamide | | Sat. in CHCl_3 | | | $(+). 6.0 \pm 0.2^1$ |
| Dimethyl 2, 2-di-methylcyclopropane- <u>trans</u> -1, 3-dicarboxylate | | 5% in CCl_4 | | | $(+). 6 \pm 0.2^1$ |
| <u>trans</u> -3-(<u>trans</u> -2'-carboxypropenyl)-2, 2-dimethylcyclopropane-1-carboxylic acid | | Sat. in CHCl_3 | | | $(+). 7 \pm 0.2^1$ |
| Methyl- <u>trans</u> -3-(<u>trans</u> -2'-carboxypropenyl)-2, 2-dimethylcyclopropane-1-carboxylate | | Sat. in CHCl_3 | | | $(+). 4 \pm 0.2^1$ |

^aAssigned on the basis that the phenyl group in phenylcyclopropane deshields the trans protons more than the cis protons.

^bMagnitudes and signs of coupling constants verified with 1-phenyl-1-bromocyclopropane in chloroform solution.

^cMagnitudes and signs of coupling constants verified with dimethyl 1-methylcyclopropane-trans-1,2-dicarboxylate in benzene solution.

^dSign assumed to be negative.

^eTaken as twice the frequency difference between the parent peak and the center of the upfield satellite.

^fIn good agreement with the value of 161 cps reported in Ref. 22.

^gAt 56.4 Mc. relative to fluorotrichloromethane.

^hChemical shift in cps from tetramethylsilane for 5% w/v solutions in carbon tetrachloride.

ⁱSign assumed to be positive.

^jObtained from ¹³C satellite spectrum.

^kChemical shift in cps from tetramethylsilane

TABLE II
SUMMARY OF CALCULATIONS OF RING CURRENT EFFECTS ON CHEMICAL SHIFTS IN CYCLOPROPANES^a

| Compound | Obsvd. | Side-chain, Δ cps | | | Cyclopropyl, Δ cps | | |
|---|-------------------|--------------------------|--------------|--------------|---------------------------|--------------|--------------|
| | | Case A 4e | Case B 6e | Case B 4e | Case A 6e | Case B 4e | Case B 6e |
| Cyclopropane | | | | | 73.2 ^b | 19.6 | 29.4 |
| Nortricyclene (CH) | 18.0 ^c | 23.4 | 34.2 | 29.4 | 43.8 | | |
| 1, 1-Dimethylcyclopropane ^d | -9.0 ^d | 12.6 | 18.6 | | | | |
| Dicyclopropylmethane ^h | 9.6 ^d | 25.2 | 37.8 | | | | |
| Spirohexane (in-plane) ^e | -6.0 | -8.4 | -12.6 | -11.4 | -17.4 | | |
| Spirohexane (out-of-plane) ^e | -6.0 | 3.6 | 6.0 | 6.0 | 9.6 | -30.6 | -3.6 |
| Spiropentane ^f | | | | | | -6.0 | -3.6 |
| | | | | | | -3.6 | -5.4 |

^a A positive value of Δ cps indicates an upfield shift while a $-\Delta$ cps indicates a downfield shift due to ring-current effect.

^b Compared with cyclohexane.

^c Bicyclo[2.2.1]heptane was taken as a model compound in which the cyclopropyl ring was absent.

^d Obtained by comparison with shifts in aliphatic hydrocarbons.

^e Cyclobutyl hydrogens coplanar or out-of-plane with the cyclopropyl ring; observed Δ cps are relative to cyclobutane.

^f Calculated Δ cps takes account of modification of ring-current due to a geometry different from cyclopropane.

^g Calculated as the average for four conformations of the C-H bond.

^h Assumed to be twice that for 1, 1-dimethylcyclopropane.

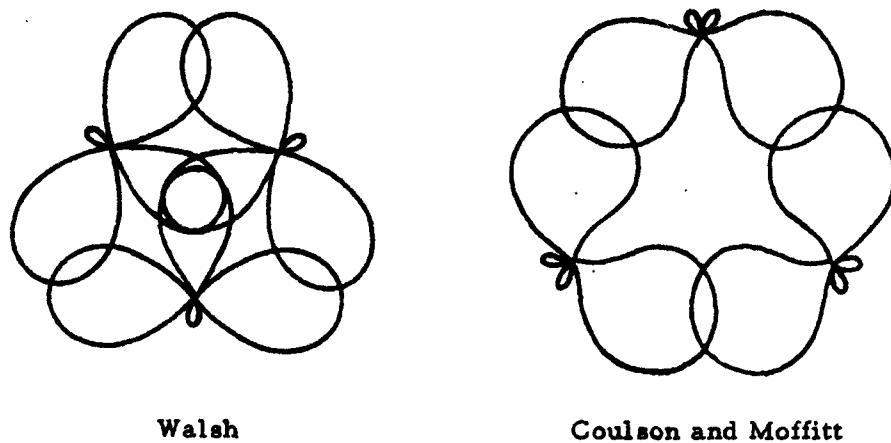


Fig. 1. - Walsh and Coulson and Moffitt orbital models for C-C bonding in cyclopropane rings.

Experimental

The 60-Mc proton n. m. r. spectra of the AB system and ABC, AA'XX', and AA'BB' systems were taken on the V-4300B and A-60 high resolution spectrometers, respectively. The chemical shifts on the V-4300B were measured by means of a Hewlett-Packard Model 200AB audio oscillator and Model 521C frequency counter. Line positions have been measured to an accuracy of 0.1 cps. Tetramethylsilane was used as an internal reference in the study of AB systems and as an external reference for other systems. Proton and fluorine ^{13}C satellite n. m. r. spectra were taken for ^{13}C in natural abundance. ^{13}C -H coupling constants were obtained as the difference between the chemical shifts of the centers of the low- and high-field satellites.

Hexafluorocyclopropane was a sample generously supplied by Dr. D. C. England of the DuPont Company. The positions of the ^{13}C -satellite peaks were determined at 56.4 Mc, using side bands from the parent difluoromethylene peak. The chemical shift of the latter peak was measured by interpolation with a 50% solution of hexafluorocyclopropane in fluorotrichloromethane, by generating an approximately 600-cps side band and sweeping rapidly through to the fluorotrichloromethane peak.

1,1-Dichlorocyclopropane was obtained by photochlorination of cyclopropane. It was distilled through a center-rod fractionating column and the fraction b. p. 74.5° (744.5 mm), $\underline{n}^{25}\text{D}$ 1.4373 (lit. 33 b. p. $74 - 75^\circ$,

(33) J. D. Roberts and P. H. Dirstine, J. Am. Chem. Soc.,
67, 1281 (1945)

$\underline{n}^{20}\text{D}$ 1.4400) was used.

1,1-Dimethylcyclopropane was prepared by Cox³⁴ and was

(34) E. F. Cox, Ph. D. Thesis, California Institute of Technology, 1955.

used without further purification.

Spiropentane of b. p. 36-38° was obtained from Professor D. E. Applequist. It had been distilled after treatment with bromine and dried over calcium hydride.

Spirohexane was furnished by Professor D. E. McGreer.³⁵

(35) D. E. McGreer, Can. J. Chem., 38, 1638 (1960).

1-Phenyl-1-bromocyclopropane was prepared in these laboratories by Dr. D. I. Schuster.

Dimethyl 1-Methylcyclopropane-cis-1, 2-dicarboxylate. - The parent diacid, m. p. 139-141°, was provided by Professor L. L. McCoy,³⁶

(36) L. L. McCoy, J. Am. Chem. Soc., 80, 6568 (1958).

and was esterified with an excess of diazomethane in benzene. The product was microdistilled at 3 mm. with a bath at 80°.

Dimethyl 1-Methylcyclopropane-trans-1, 2-dicarboxylate. - The parent diacid, m. p. ca. 170° from Professor L. L. McCoy, was esterified with excess diazomethane. The resulting dimethyl ester was microdistilled at 2 mm. with a bath at 65-70°.

Nortricyclene was a pure sample obtained from Professor H. Hart. The spectrum showed a small broad CH peak, large CH₂

peak and a cyclopropyl peak at 114. 6, 70. 8 and 57. 60 cps respectively with areas 1:6:3. The chemical shift for the cyclopropyl peak was measured by side-band superposition from tetramethylsilane, and that for the CH₂ and CH peaks by interpolation from two tetramethylsilane side bands. Since the chemical shifts were critical, they were obtained from the maxima or geometric center of each resonance for volume fractions of nortricyclene in carbon tetrachloride of approximately 1. 0, 0. 25, 0. 06, 0. 016 and extrapolating to infinite dilution.

1, 3, 4, 5-Tetramethyl-2-methylene-bicyclo[3. 1. 0]hex-3-ene was obtained from Dr. L. deVries.³⁷ Two side bands from the vinyl

(37) L. deVries, J. Am. Chem. Soc., 82, 5242 (1960).

peak were used to obtain the frequencies of the cyclopropyl peaks by interpolation, the chemical shift difference between the cyclopropyl hydrogens being 3. 9 cps. The chemical shift of the center of the cyclopropyl methylene quartet was measured by interpolation from side bands from tetramethylsilane for a 5% w/v solution of the hydrocarbon in carbon tetrachloride and found to be 31. 2 cps.

2-Oxa-7, 7-dichloronorcarane of b. p. 50-52° (1. 6-1. 9 mm.) n_D^{25. 7} 1. 4981 was provided by Professor W. E. Parham.³⁸ The n. m. r.

(38) E. E. Schweizer and W. E. Parham, J. Am. Chem. Soc., 82, 4085 (1960).

spectrum of a 5% w/v solution of 2-oxa-7, 7-dichloronorcarane in carbon tetrachloride showed two main groups of peaks, the larger group at high-field being assigned to the methylene hydrogens at C4, C5 and the cyclo-

propyl methine hydrogen at C6; and the smaller group at low-field to the methylene hydrogens at C3 and the cyclopropyl methine hydrogen at C1. The latter gave a prominent unsymmetrical doublet on the low-field side of the lower group of peaks, due to cis-vicinal spin coupling with the cyclopropyl methine hydrogen at C6. The frequencies of the peaks in this doublet were determined by side-band superposition from tetramethylsilane.

Dicyclopropylmethane was provided by Professor H. Hart.³⁹

(39) H. Hart and O. E. Curtis, J. Am. Chem. Soc., 78, 112 (1956).

The acyclic methylene resonance appeared as a broadened doublet near the cyclopropyl methine peaks. The chemical shift for the center of this doublet was obtained by extrapolation to infinite dilution and found to be 65.4 cps downfield from tetramethylsilane.

trans-3-(trans-2'-Carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid was the dextrorotatory enantiomer, m.p. 164-165°, obtained from Professor Y. Inouye.⁴⁰ The line positions were measured

(40) Y. Inouye, Bull. Inst. Chem. Res., Kyoto Univ., 35, 49 (1957); C. A., 52, 11759 (1958).

by superimposing side bands from chloroform.

Methyl trans-3-(trans-2'-carbomethoxypropenyl)-2,2-dimethylcyclopropane-1-carboxylate, m.p. 80° was also provided by Professor Y. Inouye.

2, 2-Dimethyl-trans-3-phenylcyclopropane-1-carboxylic acid
was provided by Professor F. Sorm⁴¹ and had m. p. 102°. Approximate

(41) J. Karkas, P. Kourim and F. Sorm, Chem. listy, 52, 695 (1958); C. A., 52, 13651 (1958).

chemical shifts (accurate to ± 1 cps) were obtained for the methyl and cyclopropyl hydrogens by interpolation from a tetramethylsilane peak (internal reference) and the low-field cyclopropyl doublet, which has been accurately calibrated. The chemical shift differences were thus found to be 48 cps between the cyclopropyl hydrogens and 31 cps between the gem dimethyl groups.

2, 2-Dimethyl-cis-3-phenylcyclopropane-1-carboxylic acid was also provided by Professor Sorm and had m. p. 134°. The chemical shift between the cyclopropyl hydrogens was 39 cps, and between the gem dimethyl groups only 2 cps.

2, 2-Dimethyl-trans-3-phenylcyclopropane-1-carboxamide was obtained from Professor G. W. Perold.⁴² The chemical shifts were

(42) G. W. Perold, J. S. African Chem. Inst., 10, 11 (1957).

approximately 55 cps between the cyclopropyl hydrogens and 27 cps between the gem dimethyl groups.

Dimethyl 2, 2-dimethylcyclopropane-trans-1, 2-dicarboxylate.-- The parent diacid was obtained from Professors Y. Inouye and M. Matsui, who report m. p. 210-212° and 212-213° respectively. The combined samples were esterified with excess diazomethane, and the product was

microdistilled at 14 mm. with a bath at 125-130° and gave diester of $n^{24}\text{D}$ 1.4434. The high-field cyclopropyl ^{13}C satellite was a slightly unsymmetrical doublet. The resonances were calibrated by side-band superposition from the carbomethoxyl peak.

Dimethyl 1, 2-dimethylcyclopropane-cis-1, 2-dicarboxylate was provided by Professor L. L. McCoy and contained 7% of the trans isomer. Two side bands from the methyl peaks were placed on either side of the upfield cyclopropane doublet and the splitting determined by interpolation. The analysis of the cyclopropyl methylene quartet indicated that the chemical shift between the cyclopropyl hydrogens was 79.0 cps.

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